Sborník vědeckých prací Vysoké školy báňské – Technické univerzity Ostrava
číslo 1, rok 2008, ročník LI, řada hutnická
článek č. 1421

SURFACE-ACTIVE AND VISCOMETRIC PROPERTIES OF HM-CMC SOLUTIONS

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ABSTRACT: This contribution deals with investigation of surface-active and viscometric properties of aqueous and aqueous sodium chloride solutions of unmodified CMC and their HM-CMC derivatives. Polymeric surfactants (hydrophobically modified carboxymethylcellulose (HM-CMC)) have been prepared by chemical modification of CMC with methyl ester of rape seed oil (MERO) in reaction media H_2O/DMF at various reaction conditions, under microwave irradiation with controlled power as heating source used to optimize the preparation of water-soluble esters. The surface-active properties were studied by surface tension, critical micelle concentration and emulsifying efficiency. Most of the CMC esters exhibited very positive surface-active properties such as excellent emulsification properties for 'oil in water' type emulsions, which are comparable to that of the commercial synthetic emulsifier Tween 20. Although the derivatives do not substantially lower the surface tension of water, they form micelles in the concentration range 0.3 to 2.45 $g.l^{-1}$.The viscometric properties of their aqueous sodium chloride solutions were investigated in dilute range. The viscosities decreased due to the concentration of the HM-CMC derivatives by intramolecular interactions.

KEY WORDS: carboxymethylcellulose, polymeric surfactants, associate polymers

1. INTRODUCTION

During the last decades, a fast growing interest in natural, biodegradable and renewable materials has been noticed because of the variety of their possible pharmaceutical, biotechnological and industrial applications. Carboxymethylcellulose (CMC)is the most important water-soluble anionic cellulose derivative of significant technical importance. Its commercially available in large quantities and known to act as water binder, thickener, emulsion stabilizer, suspending agent and antiredeposition agent in detergents [1]. Also represents a potential biopolymer for further modification aimed to create new advanced cellulosic materials. Recently, various alternative esterification methods have been developed with the aim to avoid the use of acid halides such as esterification with mixed anhydrides prepared "in situ" [2], transesterification with vinyl carboxylic acid esters like vinyllaurate [3] and transesterification with fatty acid methyl esters [4, 5]. In our previous papers [6, 7], attention was paid to modification of CMC by alkylation and acylation under conventional heating. Prepared derivatives of CMC were water-soluble with surface-active properties. Nowadays attention has been paid to apply the new heating system - microwave irradiation in organic and polymer chemistry [8, 9]. The most important advantage is that microwave-enhanced chemical reactions are very rapid, lasting usually a few minutes, compared to hours with classical heating methods. In continuation of our research on partial hydrophobization of CMC using transesterification with methyl ester of rape seed oil (MERO)under microwave irradiation with controlled power [10], this paper is focused on the characterization of HM-CMC solutions by surface active and viscometric measuring.

2. EXPERIMENTAL

2.1 Materials and measurements

CMC (Na^+ salt; DS_{CM} = 1; Mw = 741 kDa, Walsrode Germany).
The methyl ester of rape seed oil (MERO) was from VÚTCH-Chemitex s.r.o. (Žilina, Slovakia). It contains oleic acid (58 %), linoleyl acid (17 %), linolenyl acid (17 %) and saturated C_{14-20} fatty acids (8 %).
Tween 20 was from Aldrich Chemical Co. (Steinheim, Germany).
Synthesis has been carried out in microwave reactor 'Milestone' (maximum 1000 W power) equipped with a magnetic stirrer (Sorisole, Italy).
Fourier-transform infrared (FT-IR) spectra were obtained on the NICOLET Magna 750 spectrometer with DTGS detector and OMNIC 3.2 software using 128 scans at a resolution of 4 cm^{-1}. The samples (2.0 mg) were pressed into pellets of KBr (200 mg).
Viscometric measurements were carried out using Ubbelohde - type capillary viscometers (0,64 diameter).

2.2 Methods

2.2.1 Modification of CMC by esterification with MERO

The HM-CMC derivatives were obtained by modification of CMC with MERO in H_2O/DMF under microwave irradiation [10].
CMC (1.0 g) was solubilized in 25 ml H_2O under stirring at room temperature for 1 h. Subsequently, MERO (1.0-3.0 g) in 25 ml DMF was added to the CMC solution. The reaction mixture, with and without addition of K_2CO_3 (0.07 g in 5 ml water) as catalyst, was under permanent stirring exposed to microwave heating in two stages. In the first stage lasting 5 min the power was increased from 0-300 W and the temperature increased from room to reaction temperatures (90-110 °C). In the second stage (300 W power) the reaction continued at the selected reaction temperature and measuring of the reaction time started. After reaction, the product was poured into 4-6 volumes of acetone and the precipitated derivative was separated by filtration, thoroughly washed with acetone, and extracted in a Soxhlet apparatus with acetone for 8 h. The HM-CMC derivatives were obtained in the carboxylate form and were water-soluble. The FTIR spectra of the HM-CMC derivatives showed an absorption band or shoulder at 1730 cm^{-1} indicating the presence of ester linkages. Reaction conditions and yields of some derivatives used for subsequently solution characterization are given in Tab. 1.

Tab. 1: Reaction conditions and yield of selected MH-CMC derivatives prepared in the H_2O/DMF medium at controlled power 300 W.

Sample	CMC:MERO [Mass ratio]	Reaction time[b] [min]	Temperature [°C]	Yield [g/g][c]
I	1:1	1	90	1.03
II	1:1	2	90	1.03
III	1:2	1	90	1.03
IV	1:2	2	90	0.87
V[d]	1:1	2	90	1.03
VI[a]	1 : 1	1	90	1.11
VII[a]	1 : 2	1	90	0.99
VIII[a]	1 : 2	3	90	1.02
IX[a]	1 : 2	5	90	1.12
X[a]	1 : 2	3	105	1.11
XI[a]	1 : 1	2	90	0.92

a) K_2CO_3 was used as catalyst
b) Measured after the 1st stage of microwave heating;
c) Expressed as g of the recovered derivative per g CMC (on dry mass basis);
d) The 1st stage lasted only 3 min;

2.2.2 Surface-active properties of MH-CMC derivatives

All derivatives were characterized by emulsifying efficiency. The emulsifying efficiency was tested on emulsion of the 'oil in water' (O/W) type. The emulsion was prepared by mixing 9 ml water containing 0.05 g of the CMC derivative and 1 ml of paraffinic oil dyed with SUDAN IV in the laboratory mixer (Heidolph DIAX 600) at 20 500 rpm for 1 min. The stability of the emulsion was estimated at three different time intervals after the emulsions had been prepared, i. e. 5 min (h_1), 1 h (h_2) and 24 h (h_3), and expressed in terms of the height (mm) of the oil and cream layers formed on the surface of the emulsion.
The surface tension of aqueous polysaccharide solution in the concentration range 0.015-5.0 $g.l^{-1}$ was determined at 25 °C using the Du Nouy ring apparatus. Surface tension data were plotted against the logarithm of polysaccharide concentration in order to obtain the critical micelle concentration (c.m.c.) and minimum surface tension (γ_{min}), as described in previous papers [7, 11]. Some results are given in Tab. 2.

Tab. 2: Surface-active properties (surface tension, γ_{min}, critical micelle concentration, c.m.c., emulsifying efficiency) of selected MH-CMC derivatives and controls.

Sample	γ_{min} [$mN.m^{-1}$]	c.m.c. [$g.l^{-1}$]	Oil / Cream layers[a] (mm/mm)		
			h_1	h_2	h_3
I	55	0.32	0/0	0/10	0/9
II	-	-	0/0	0/0	0/7
III	46.6	2.45	0/0	0/0	0/6
IV	62.9	1.77	0/0	0/0	0/6
V	54.1	0.79	0/0	0/0	0/7
VI	45.6	No	0/0	0/1	0/4
VII	58.1	1.25	0/0	0/11	1/9
VIII	49.9	0.74	0/0	0/0	0/5
IX	50.4	2.04	0/0	0/0	1/7
X	46.5	No	0/0	0/0	0.5/9
XI	47.5	1.78	0/0	0/10	8/2
CMC	65.8	0.75	0/0	0/0	0/3
Tween 20	-	-	0/0	0/0	0/8
SDS	32	1.25	-	-	-

a) Height of oil and cream layers formed on the surface of the emulsion after 5 min (h_1), 1 h (h_2) and 24 h (h_3);
(-) Not determined.
SDS – Sodium dodecyl sulphate

2.2.3 Viscosity properties of HM-CMC derivatives

The soluntions behaviour of HM-CMC derivatives can be also described by viscometric experiments. The viscometric measurements with sodium aqueous polymer solutions were carried-out using a Ubbelohde –type capillary viscometer (0.64 diameter). The temperature was regulated by a circulating bath at 25°C. The concentrations polymer solutions ranged between 0.32-0.0886 $g.dl^{-1}$. Prior to measurements, the polymer solutions were filtered through 0.2 mm filters.

The reduced viscosity η_{red} of dilute solution of polymer changes with the concentration, according to the Huggins relationship:

$\eta_{red} = \eta_{sp}/c = [\eta] + k_H.[\eta]^2.c$

where k_H is the Huggins constant depending on the nature of the polymer interaction in solutions. This equation allows the determination of k_H and intrisic viscosity (η) by plotting the reduced viscosity $\eta_{red} = \eta_{sp}/c$ as a function of polymer concentration (fig.1) Huggins constant is generally around 0,4 for non-interacting macromolecules and in good solvent can reach values above 5 for highly interacting macromolecules. For unmodified CMC (DS-0.9) in 0.1 M NaCl, the Huggins coefficient is close to 0.5 which is consistent with the results of Charpentier [12]. A similar value is found for chitosan in water [13] and for dextran in water [14].

The intrisic viscosities and Huggins constant were determined for unmodified CMC and selected HM-CMC derivatives (Tab. 3). For each modified polymer solution in dilute range, the intrinsic viscosities are distinctly lower than for the unmodified CMC and k_H remains very small, suggesting intramolecular interaction. The decrease of intrinsic viscosities of HM-CMC could be ascribed to a coil contraction or a molecular weight degradation of CMC in H_2O/DMF subjected to microwave irradiation, or a combination of both.

Tab. 3: Viscometric results obtained with HM-CMC derivatives, in aqueous sodium chloride medium at 25°C

Sample	k_H	η [dl/g]
I	0.23	6.861
II	0.21	6.151
III	0.35	6.186
IV	0.95	1.986
V	0.35	5.810
VI	0.31	8.453
VII	0.71	5.186
VIII	0.81	4.320
IX	1.06	4.101
X	0.38	8.696
XI	0.48	5.148
CMC	0.2	10.256
CMC_{mw}	0.23	8.53

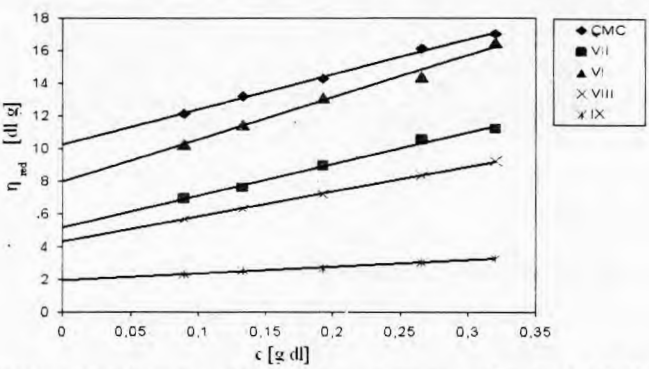

Fig.1: Reduced viscoties as a function of the polymer concentration, in 0.1 M NaCl for CMC and HM-CMC derivatives (VI, VII, VIII, IX)

3. CONCLUSIONS

The partial hydrophobization of CMC performed by transesterification reaction with MERO in H_2O/DMF system without and with catalyst at various reaction conditions yielded water-soluble amphiphilic CMC esters. Inspite of the low degrees of esterification, most of the tested CMC derivatives showed excellent emulsifying activity for oil/water type emulsion comparable to that of the commercial synthetic emulsifier Tween 20, although they had no substantially lower the surface tension of water (γ_{min}). The γ_{min} values ranged between 50-63 $mN.m^{-1}$. Exeptions are derivatives VI and X, which lowered the surface tension of water from 72.8 to ~ 46 $mN.m^{-1}$. Moreover, they form micelles in the concentration range 0.3 to 2.45 $g.l^{-1}$ except derivatives VI and X. The viscometric measurement indicate that the incorporation of hydrophobic substituents induces intramolecular associations in dilute solutions. The results substantiate the importance of CMC partially hydrophobized by transesterification methode with MERO under microwave assistance as novel polymeric surfactants with potentional industrial application.

Acknowledgements: *This work was financially supported by the Slovak Grant Agency VEGA, grant No. 2/6131/6, the Center of Excellence of the Slovak Academy of Sciences and the Agency for Support of Science and Research, project APVT - 20 – 017304, CUGA 3/2006 and CUGA 4/2006.*

3. REFERENCES

[1] FEDDERSEN, RL., THORP, SN.: *Sodium carboxyhylcellulose*, In: WHISTLER, RL. and BEMILLER JA (ed)) *Industrial Gums, Polysaccharides and their Derivatives*, Academic Press, SAN DIEGO NEW YORK BOSTON, 537, 199, 1993.

[2] VACA-GARCIA,C., BORREDON, M. E.: *Bioresource Technol,* 70, 135, 1999.

[3] HEINZE, T., DICKE, R., KOSCHELLA, A., KULL, A., KLOHR, E. A., KOCH, W.: *Macromol Chem Phys* 20, 1627, 2000.

[4] ROONEY, M. L.: *Polymer,* 17, 555, 1976.

[5] GIRARDEAU S., ABURTO, J., VACA-GARCIA, C., ALRICH, I., BERREDON, E.: *A performing method of transesterifiaction of cellulose and amylose,* IV European Symp. In Industrial Crops and Products, Bonn,129, 1999.

[6] SROKOVÁ, I., TOMANOVÁ, V., EBRINGEROVÁ, A., MALOVÍKOVÁ, A., HEINZE, T.: *Macromolecular Materials and Engeniering,* 289, 63 – 69, 2004.

[7] SROKOVÁ, I., TALABA, P., HODUL, A., BALAŽOVÁ, T.: *Tenside Surf. Det,* 35, 1998, 342.

[8] GALEMA, SA., *Chemical Chemical Society Reviews*, 26, 233, 1997.

[9] BOGDAL, D., PENCZEK, P., PIELICHOWSKI, J., PROCIAK, A.: *Adv Polym Sci* , 163:194, 2003.

[10] TOMANOVÁ, V., PIELICHOWSKI, K., SROKOVÁ, I.,ŽOLDÁKOVÁ, A., POLACZEK, J., PIELICHOWSKI, J., In: Pielichowski, K., (ed) *Modern Polymeric Materials for Environmental Applications*, Wydavnictwo DjaF, Krakow, vol. 2, 31-36, 2006.

[11] SROKOVÁ, I., EBRINGEROVÁ, A., HEINZE, T.: *Tenside Surf Det*, 38, 277, 2001.

[12] CHARPENTIER, D., MOCANU, G., CARPOV, A., CHAPELLE, S., MERLE, L., MULLER, G.: *Carbohydr Polym* 33, 177,1997.

[13] DESBRIERES, J.: *Biomacromolecules,* 3, 342, 2002.

[14] GÛNER, A.: *J App. Polym Sci,* 72, 871, 1999.